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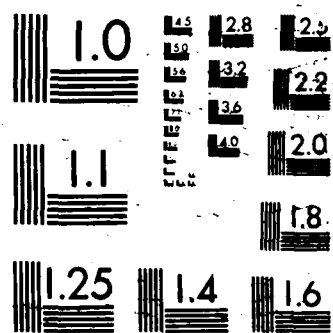
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GENERATION OF PHOSPHORUS ESTER, PHOSPHORUS AMIDE,
AND PHOSPHINE DERIVATIVES OF LOW COORDINATION NUMBER

FINAL REPORT

LOUIS D. QUIN

OCTOBER 15, 1986

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Research Triangle Park, NC 27709
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Duke University
Durham, NC 27706

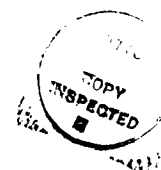
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I. Purpose of the Research Program

The 7-phosphanorbornene system is synthetically readily approached, and because of the considerable strain involved in the bridged structure, along with a mechanism provided by the double bond for a retro-cycloaddition process, this system was considered as a potential precursor of a variety of phosphorus species with low coordination numbers. The ring strain is known to permit the insertion of oxygen into a C-P bond, thus creating another ring system potentially capable of undergoing a retro[4+2] cycloaddition to release a phosphoryl compound of low coordination. A further extension of this concept could result in the synthesis of species with C-P double bonds, from the phosphabicyclo[2.2.2]octene system. To explore these possibilities, syntheses of suitable precursors are required. This report summarizes work both on the precursor syntheses, as well as on the successful generation of certain low-coordination species.

This is a report covering only the first seven months of a three-year grant period, and hence the accomplishments during this brief period are not numerous. This report is required by the transfer of the grant from Duke University to the University of Massachusetts.

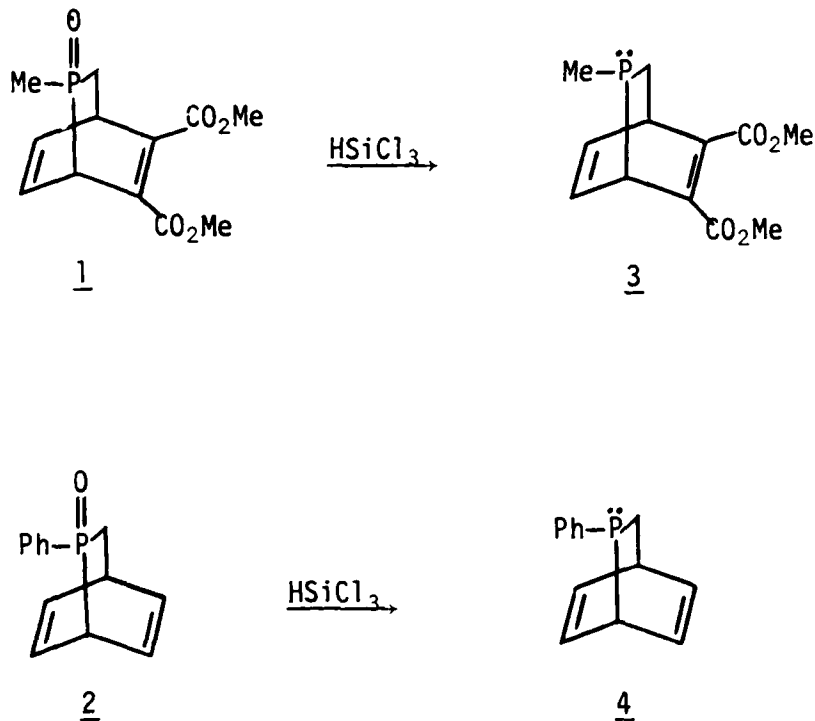
II. Major Accomplishments

A. Synthesis of a Phosphaalkene Generator

In previous work on this project, the synthesis of compounds 1 and 2 was accomplished. Preliminary work on their reduction to the corresponding phosphines 3 and 4 was not very successful, as decomposition of the phosphines accompanies their formation. We have now discovered conditions that allow the isolation of phosphine 3. The reduction may be smoothly

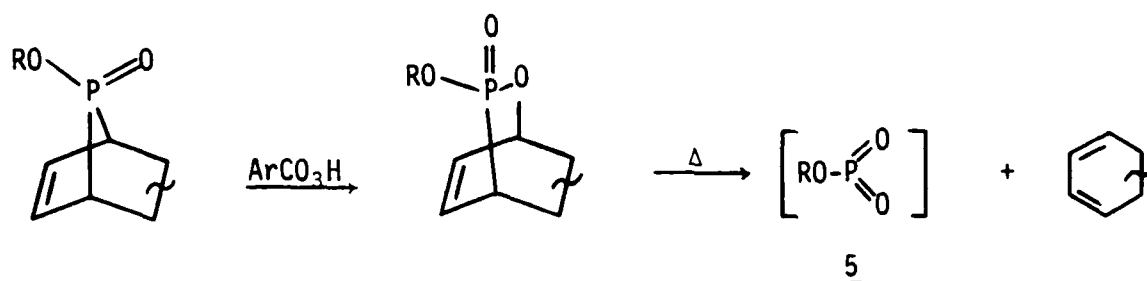
accomplished with trichlorosilane in chloroform at 15° or in benzene at 0°. These very mild conditions prevent the premature fragmentation of the phosphine, which ends up with the formation of Me₂PH and dimethyl phthalate. Phosphine 3 has δ ³¹P -37 and gives the expected ¹³C NMR spectrum. It is now available for studies on its thermal degradation, which is expected to proceed by a retro-cycloaddition to form CH₃P=CH₂ and the phthalate. The phosphalkene will be highly reactive, and its formation must be confirmed by trapping experiments. Attempts to observe it in the gas phase at low pressure by photoelectron spectroscopy will be made in collaboration with Prof. N. Werstiuk, McMaster University.

Phosphine 4 has also been formed but in poor yield. It is much less stable and has not been fully characterized. It will be less useful as a precursor of a phosphalkene.

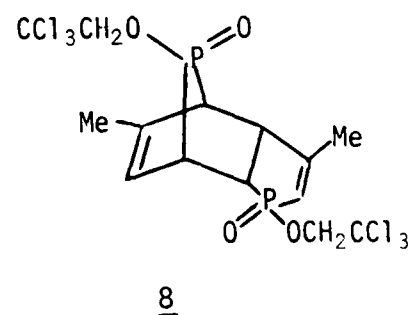
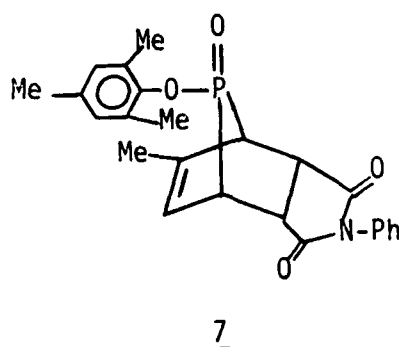
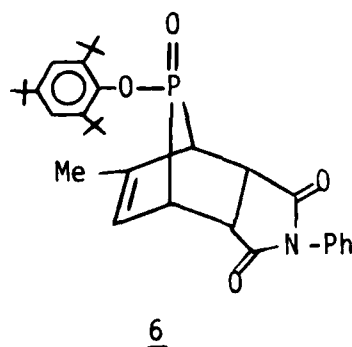


B. Synthesis of Metaphosphate Generators

The sequence below is now well established as a means for generating the highly reactive metaphosphate species (5).



In continuing our studies on this process and on the properties of metaphosphates, we have carried out the synthesis of the three new compounds 6, 7, and 8. The first two should provide a precursor after the O-insertion reaction for metaphosphates that might be stabilized by the large bulky substituent on O. Compound 8 is of interest in providing a metaphosphate with a highly desirable O-substituent in the event that the metaphosphate finds utility as a phosphorylating agent in the nucleotide field.



The very larger tri-t-butylphenyl substituent of 6, however, completely prevented the O-insertion reaction, and no way has been found to overcome this problem. The synthesis of the mesityl derivative 7 has now been accomplished but the O-insertion has not yet been attempted. Compound 8 behaved well in the O-insertion process, although it proved to be surprisingly sensitive to water. Its decomposition to $\text{CCl}_3\text{CH}_2\text{OPO}_2$ proceeded smoothly and this species was detected by the usual device of trapping with alcohol or N-methylpyrrole.

III. Publications Resulting from this Grant

1. L. D. Quin and G. Keglevich, "Stereochemistry of the Reaction of Oxygen Nucleophiles with a Phosphinous Chloride in the 7-Phosphanorbornene Series," J. Chem. Soc. Perkin Trans. II, 1029 (1986).
2. L. D. Quin and J. Szewczyk, "7-Phosphanorbornene Derivatives as Precursors of Esters and Amides of Two-coordinate Thiophosphenous O-Acid," J. Chem. Soc. Chem. Commun., 844 (1986).

IV. Participating Scientific Personnel

1. L. D. Quin, Research Director, 15 December 1985 - 31 July 1986
2. Jerzy Szewczyk, Postdoctoral Research Associate, 1 January 1986 - 30 June 1986.
3. Bela Pete, Postdoctoral Research Associate, 1 April 1986 - 31 July 1986.

IV. Participating Scientific Personnel (cont.)

4. Janell Boyd, Secretary, 20 December 1985 - 14 March 1986.
5. Robert Topping, Graduate Student, Research Assistant, 1 January 1986 - 31 March 1986
6. Brian Marsi, Graduate Student, Research Assistant, 1 May 86 - 31 August 1986
7. Xiao-Ping Wu, Graduate Student, Research Assistant, 1 May 1986 - 31 July 1986
8. Adrienne Lawler, Undergraduate Student, 12 May 1986 - 8 June 1986

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